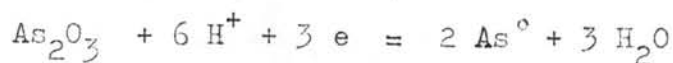




CHAPTER III

DIFFERENTIAL PULSE POLAROGRAPHIC ANALYSIS OF As (III)

The differential pulse polarographic behavior of As (III) as arsenite ion was studied in the following electrolytes: 0.1 M HCl, 0.5 M HCl, 1.0 M HCl, 2.0 M HCl, 3.0 M HCl, 6.0 M HCl, 1.0 M H₂SO₄, 1.0 M HNO₃, 0.1 M KCl and 0.1 M KNO₃. Some of these differential pulse polarograms of As (III) as arsenite ion are shown in Figure 6. Three reduction peaks were obtained in 1.0 M H₂SO₄ and HCl at various concentrations except 6.0 M HCl. The first and the last peaks were due to the reduction to As⁰ and the further reduction to AsH₃ as reported by Myers and Osteryoung (55). The reactions are as followed (60):



The middle peak was a polarographic maximum which disappeared at lower arsenic concentrations as mentioned by Myers and Osteryoung (55). No reduction peak of arsenite ion was shown in 0.1 M KCl and 0.1 M KNO₃ (see Figure 6). The DPP data of this study are shown in Table 4. In HCl, it was found that as the concentration of the acid

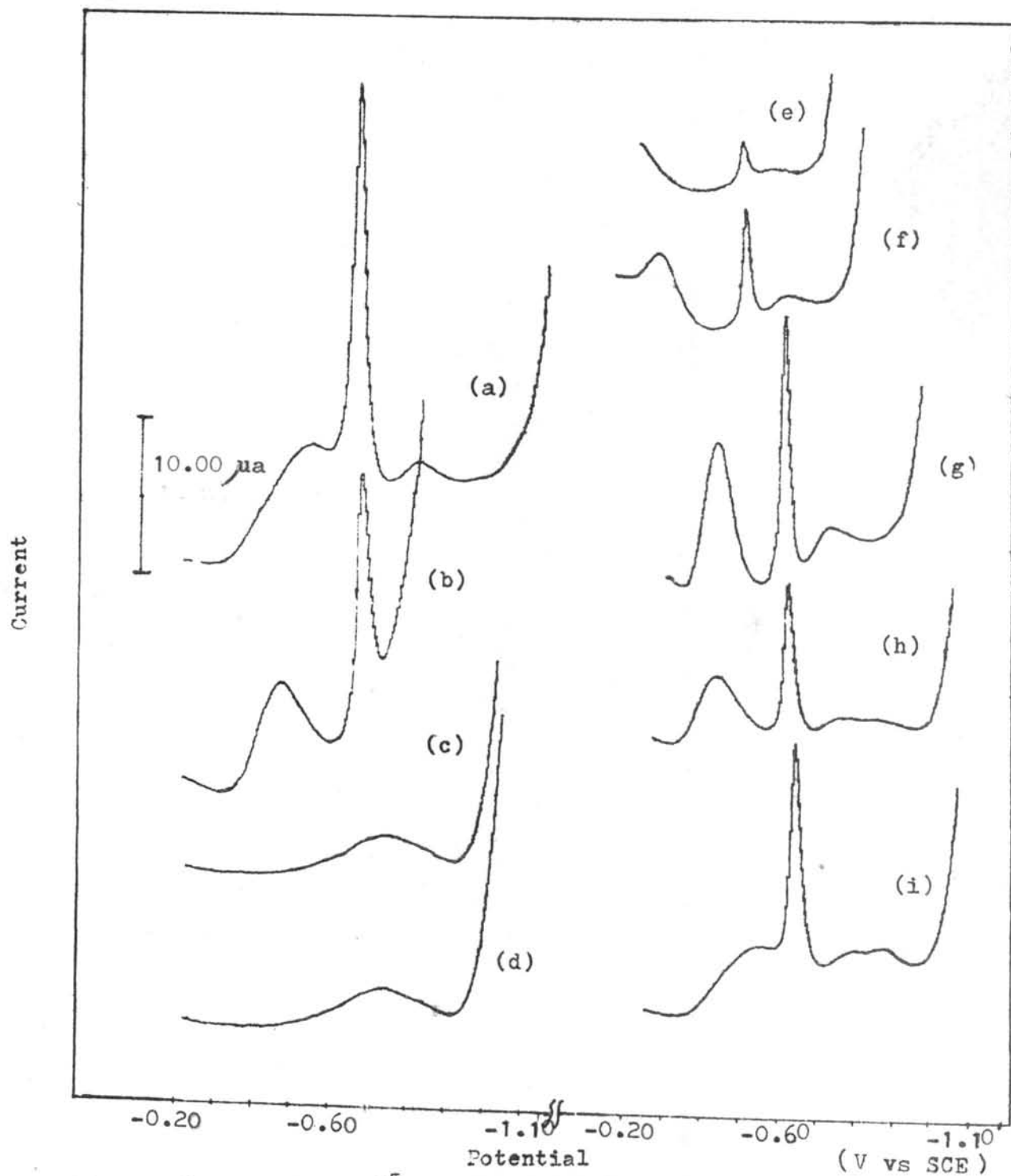


Figure 6 DPP of $5 \times 10^{-5} \text{ M}$ arsenite solution in (a) $1.0 \text{ M H}_2\text{SO}_4$, (b) 1.0 M HNO_3 , (c) 0.1 M KCl , (d) 0.1 M KNO_3 , (e) 6.0 M HCl , (f) 3.0 M HCl , (g) 1.0 M HCl , (h) 0.5 M HCl and (i) 0.1 M HCl .

Table 4 DPP data of 5×10^{-5} M arsenite solution in some supporting electrolytes

Supporting electrolyte	Peak potential(V)			Peak current(μ a)	
	First	Maximum	Second	First	Second
0.1 M HCl	-0.53	-0.64	-0.76	1.37	0.59
0.5 M HCl	-0.43	-0.61	-0.74	4.69	0.78
1.0 M HCl	-0.42	-0.59	-0.71	9.18	1.76
2.0 M HCl	-0.33	-0.51	-0.63	7.42	1.56
3.0 M HCl	-0.26	-0.48	-0.60	2.73	0.68
6.0 M HCl	none	-0.47	-0.54	none	0.20
1.0 M H_2SO_4	-0.53	-0.64	-0.81	1.76	1.17
1.0 M HNO_3	-0.47	-0.67	none	8.29	none
0.1 M KCl	N.R.	N.R.	N.R.	N.R.	N.R.
0.1 M KNO_3	N.R.	N.R.	N.R.	N.R.	N.R.

N.R. = No reaction

increased the reduction peaks of As (III) as arsenite ion shifted to less negative potentials. In 1.0 M HNO_3 , only the first two peaks were observed. From Figure 6, it was clearly demonstrated that the best supporting electrolyte studied was 1.0 M HCl since the first peak was separated from the maximum, the second peak and the cathodic background to the largest extent. Furthermore, the peak current of the first peak was higher in 1.0 M HCl than in other electrolytes as compared in Table 4 .

Throughout this study, peak currents were measured from the first peak since this peak was sharper and higher than the second one. In addition, DPP analyses of As (III) as arsenite ion were carried out in 1.0 M HCl supporting electrolyte.

In order to determine trace amount of arsenic, a series of arsenite solutions in the concentrations less than $20.00 \mu\text{g As/cm}^3$ was investigated by DPP . The results are shown in Table 5 . The lowest concentration that could be detected was $0.10 \mu\text{g As/cm}^3$. In 1.0 M HCl supporting electrolyte, the second peak disappeared when arsenite concentrations were less than $1.00 \mu\text{g As/cm}^3$ (see Figure 7). From Figure 8 , one can see that the peak current at the peak potential is directly proportional to arsenite concentration in the range of $0.10 - 20.00 \mu\text{g As/cm}^3$. Therefore, the evaluation of arsenic concentration by standard addition is available since the method can be used

Table 5 Data of DPP analysis of As (III) as arsenite ion in 1.0 M HCl supporting electrolyte at the reduction potential of -0.42 V

Concentration ($\mu\text{g As/cm}^3$)	i_p^* (μa)	Concentration ($\mu\text{g As/cm}^3$)	i_p^* (μa)
0.10	0.01 ± 0	4.00	3.66 ± 0.04
0.20	0.06 ± 0	6.00	4.65 ± 0.06
0.30	0.10 ± 0	7.00	6.45 ± 0.03
0.40	0.25 ± 0	8.00	8.59 ± 0
0.50	0.31 ± 0.01	9.00	9.47 ± 0.19
0.60	0.41 ± 0	10.00	9.94 ± 0.04
0.70	0.55 ± 0	12.00	12.89 ± 0
0.80	0.66 ± 0	14.00	16.01 ± 0
0.90	0.82 ± 0.01	16.00	17.72 ± 0.20
1.00	0.99 ± 0.01	18.00	20.51 ± 0
3.00	2.67 ± 0.01	20.00	20.79 ± 0.20

* average peak current \pm average deviation of 4 trials

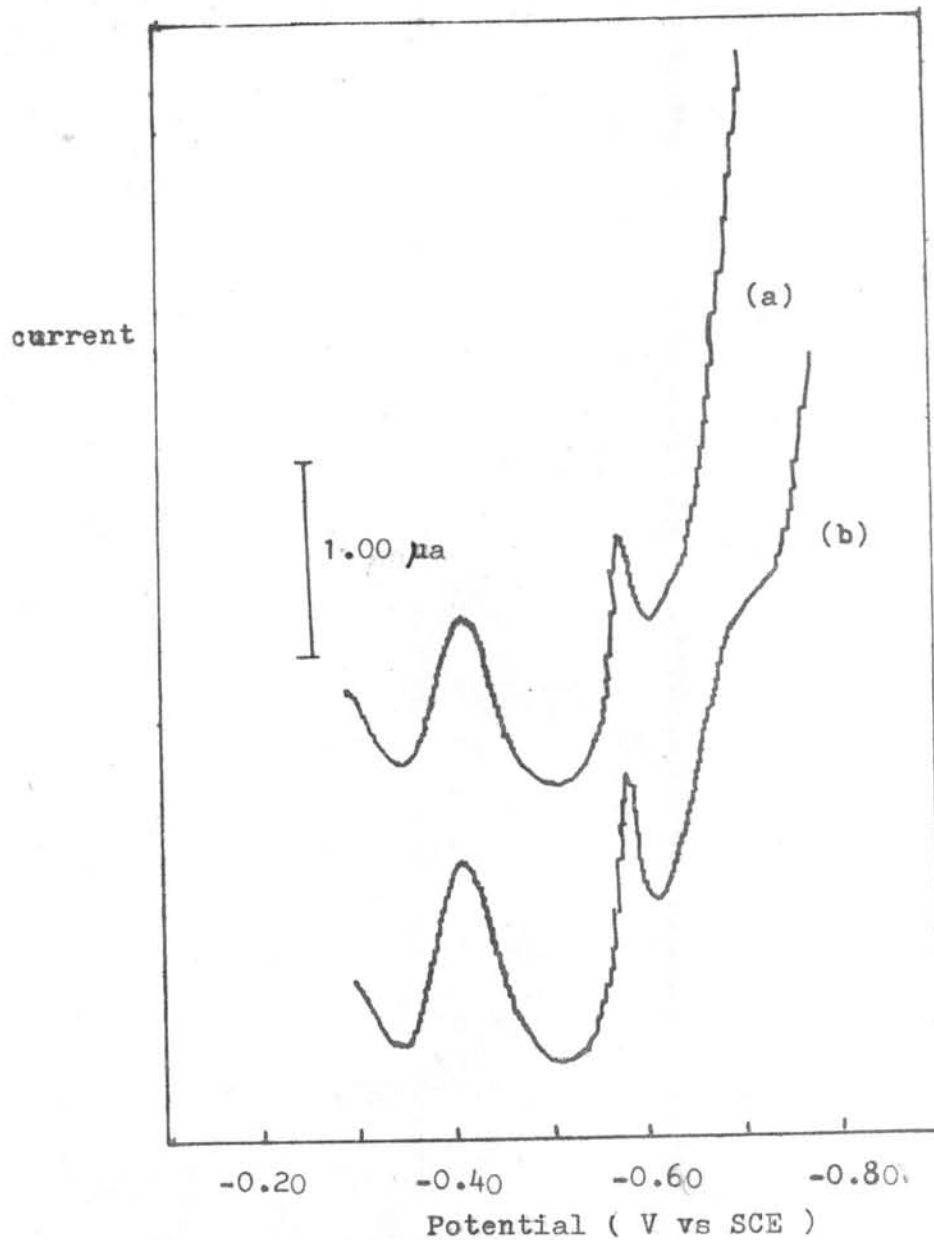


Figure 7. DPP of arsenite ion showing the disappearance of the second peak when its concentration is less than $1.00 \mu\text{g As/cm}^3$:

(a) DPP of $0.90 \mu\text{g As/cm}^3$

(b) DPP of $1.00 \mu\text{g As/cm}^3$

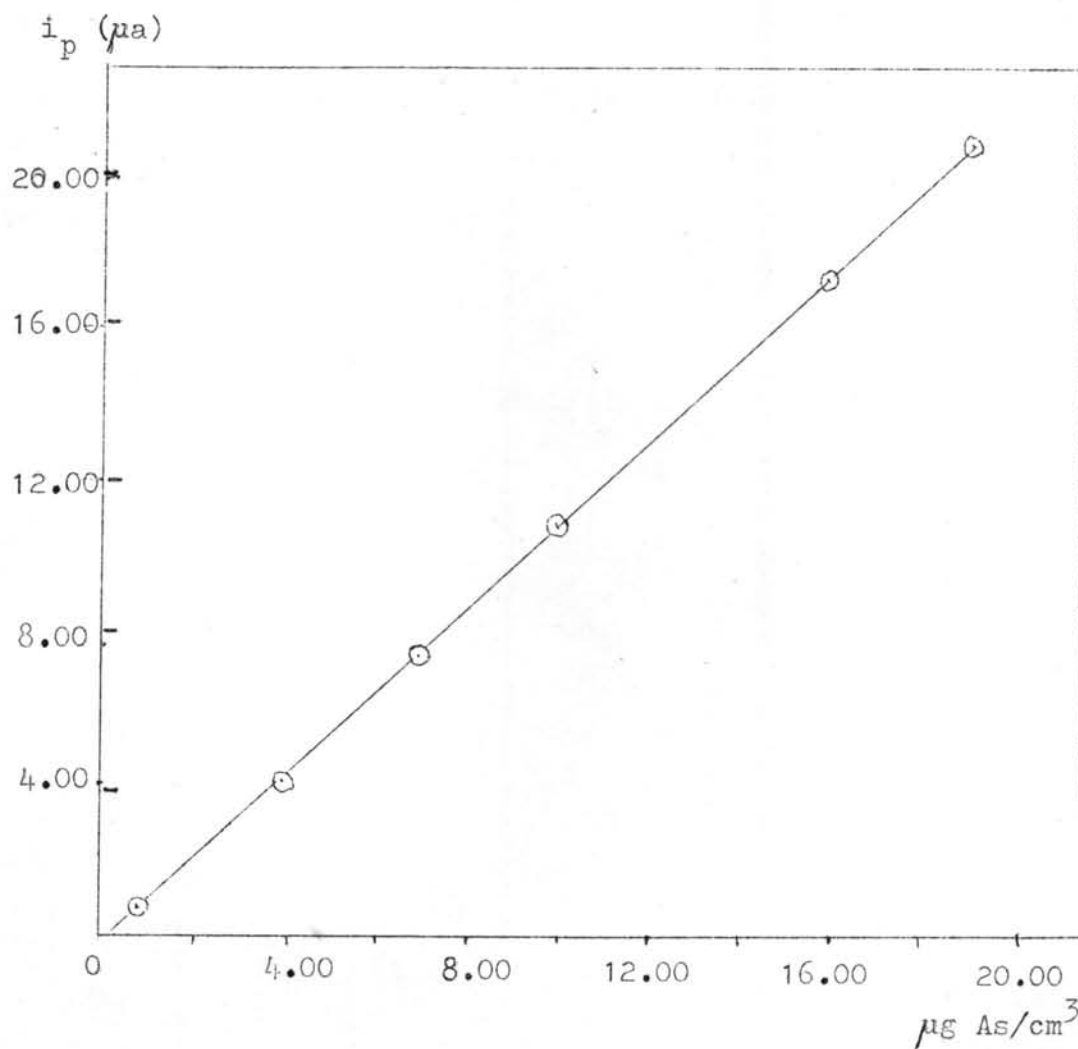


Figure 8. Linear dependence of peak currents on concentrations for DPP analysis of As (III) in the range 0.10-20.00 $\mu\text{g As/cm}^3$. The line obtained from least squares method.

only if the concentration is rectilinear with the peak current.

In 1.0 M HCl supporting electrolyte, only Pb (II) ion seriously interferes since both As (III) and Pb (II) are reduced at nearly the same potential, i.e. - 0.42 and - 0.47 volts vs SCE, respectively (see Table 6 and Figure 9). A separation method should be performed to remove the interference. EDTA (ethylenediaminetetraacetic acid) which was capable for eliminating this interfering (51), was found to be unsuccessful in shifting the reduction potentials of As (III) and Pb (II) separately. Ion exchange techniques were also investigated. The anion exchange studies of arsenic by Nelson and Kraus showed that in HCl medium, arsenic formed negatively charged complexes which were adsorbed on anion exchange resin (61). This was experimentally proved with Amberlite IR - 400 (OH) (see Table 7). The arsenite solutions were prepared in such a manner that they were in 0.1 M HCl medium or 1.0 M HCl medium when they were treated with the anion exchange resins, and in DPP analysis they were in 1.0 M HCl supporting electrolyte. In the medium of 0.1 M HCl, arsenite ion at the concentration of $5 \mu\text{g As/cm}^3$ was totally adsorbed on the anion exchanger. At higher concentration of HCl arsenite ion was partially adsorbed by Amberlite IRA - 400 (OH). So anion exchange resin cannot be used in removing the interference.

Table 6 DPP data of Pb (II) ion and As (III) as arsenite ion in 1.0 M HCl

Solution	E_p (V)	i_p^* (μ a)
2.50 μ g As/cm ³	-0.43	2.39 \pm 0.04
2.00 μ g Pb/cm ³	- 0.47	1.44 \pm 0
2.50 μ g As/cm ³ and 2.00 μ g Pb/cm ³	-0.46	4.15 \pm 0

Table 7 The comparison of DPP data of As (III) as arsenite ion in 1.0 M HCl with and without the use of Amberlite IRA-400 (OH)

Solution	Ion exchange medium	i_p^* (μ a)	
		Without resin	With resin
5.00 μ g As/cm ³	0.1 M HCl	0.80 \pm 0	0
5.00 μ g As/cm ³	1.0 M HCl	5.02 \pm 0.09	2.24 \pm 0.03

* average peak current \pm average deviation of 4 trials

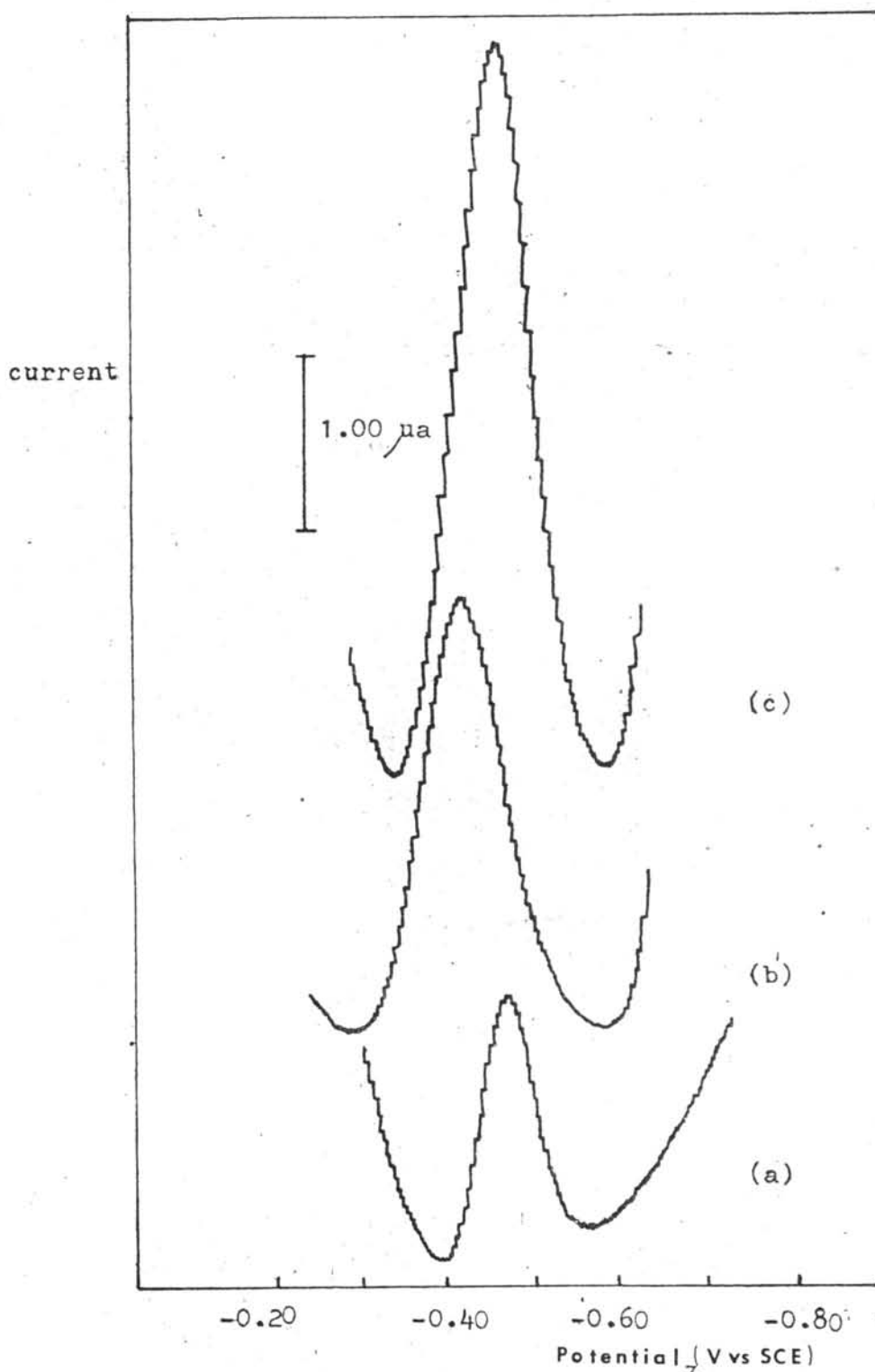


Figure 9. DPP of (a) $2.00 \mu\text{g Pb/cm}^3$, (b) $2.50 \mu\text{g As/cm}^3$, and (c) $2.00 \mu\text{g Pb/cm}^3 + 2.50 \mu\text{g As/cm}^3$.

Cation exchange behavior of As (III) as arsenite ion and Pb (II) ion was also studied (see Table 8). The standard solutions of both As (III) and Pb (II) ions were prepared so that they were in 0.1 M HCl, 0.5 M HCl or 1.0M HCl medium when they were treated with the cation exchange resins and when they were subjected to DPP analysis they were in 1.0 M HCl supporting electrolyte. For As (III) as arsenite ion, there was no adsorption of arsenite ion by Amberlite IR - 120 (H) in the mediums studied which were 0.1 M HCl, 0.5 M HCl and 1.0 M HCl. It was discovered that in 0.1 M HCl medium, Pb (II) ion was totally adsorbed by Amberlite IR - 120 (H). When the concentrations of HCl increased the adsorption of Pb (II) ion decreased. It was explained that the selectivity coefficient of Pb (II) ion decreased as pH decreased (62). The results obtained were agreeable to the separation of arsenic by cation exchanger as described by Odencrantz and Reiman (63). Figure 10 (a) shows the DPP of $5.00 \mu\text{g Pb/cm}^3$ without any treatment with cation exchange resins. Figure 10 (b) shows the DPP of the mixture of As (III) as arsenite ion and Pb (II) ion in the ion exchange medium of 0.1 M HCl with no treatment with cation exchanger where Figure 10 (c) is the DPP of the same mixture after the treatment with cation exchangers. Since the exchange capacity of Amberlite IR - 120 (H) is 5.0 meq/g of dry resin, the amount of 20.0 g of resins is enough to remove $20.0 \mu\text{g Pb/cm}^3$ of

Table 8 The comparison of DPP data of As^(III) as arsenite ion and Pb (II) ion in 1.0M HCl with and without the use of Amberlite IR - 120 (H)

Solution	Ion Exchange Medium	i_p^* (μ a)	
		Without resin	With resin
5.00 μ g Pb/cm ³	0.1 M HCl	3.54 \pm 0.08	0
5.00 μ g Pb/cm ³	0.5 M HCl	4.04 \pm 0.01	0.10 \pm 0
5.00 μ g Pb/cm ³	1.0 M HCl	7.93 \pm 0.02	4.02 \pm 0
5.00 μ g As/cm ³	0.1 M HCl	0.88 \pm 0	0.88 \pm 0.01
5.00 μ g As/cm ³	0.5 M HCl	5.04 \pm 0	5.02 \pm 0.02
5.00 μ g As/cm ³	1.0 M HCl	6.11 \pm 0.01	6.10 \pm 0.01
5.00 μ g As/cm ³ and 5.00 μ g Pb/cm ³	0.1 M HCl	4.52 \pm 0.02	0.88 \pm 0.01

* average peak current \pm average deviation of 4 trials

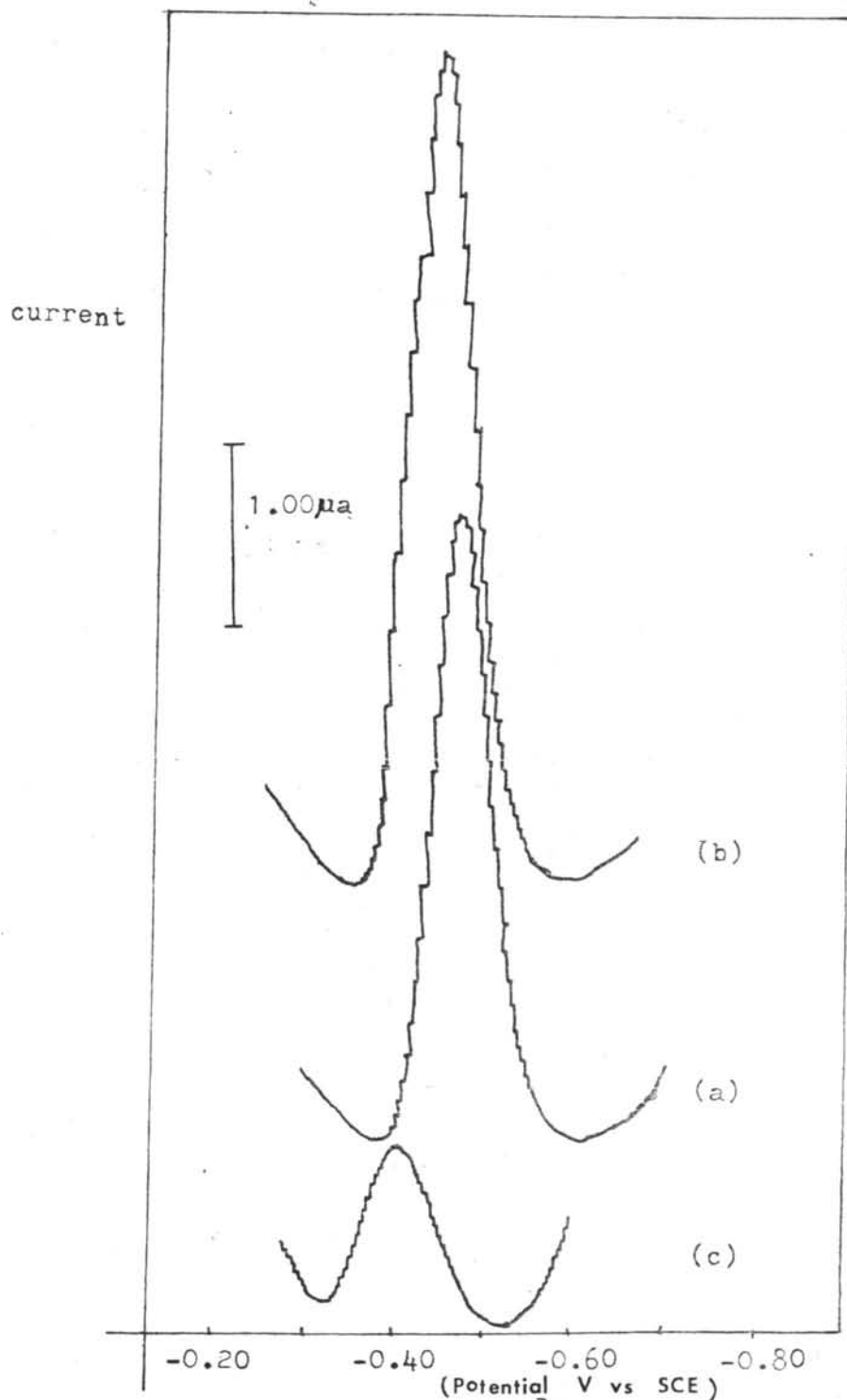


Figure 10. DPP of (a) $5.00 \mu\text{g Pb/cm}^3$ without the cation exchange resin treatment, (b) $5.00 \mu\text{g Pb/cm}^3 + 5.00 \mu\text{g As/cm}^3$ without the cation exchange resin treatment, and (c) solution (b) with the cation exchange resin treatment.

the sample solution. By using the average value of the conversion factors of the fresh weight and dry weight of vegetables (i.e. 15) as reported in the next chapter together with the exchange capacity of the resins used, the calculated amount of Pb (II) ion that could be removed was about 3,000 $\mu\text{g}/\text{kg}$ of fresh vegetable. The maximum Pb content found in vegetables grown in Bangkok Metropolitan and nearby was reported to be none to 113.35 $\mu\text{g}/\text{kg}$ of fresh vegetable (64). Therefore, the resin in amount of 20.0 g can eliminate interfering Pb (II) ion.

As a result, the following DPP analyses of arsenic were performed in 1.0 M HCl supporting electrolyte. Prior to each determination, the interfering Pb (II) ion had been eliminated by Amberlite IR - 120 (H) in 0.1 M HCl ion exchange medium.